

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
6 May 2004 (06.05.2004)

PCT

(10) International Publication Number  
**WO 2004/037715 A2**

- (51) International Patent Classification<sup>7</sup>: **C01B**
- (21) International Application Number: PCT/US2003/021692
- (22) International Filing Date: 11 July 2003 (11.07.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
60/395,327 12 July 2002 (12.07.2002) US
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- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**  
— without international search report and to be republished upon receipt of that report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: LOW TEMPERATURE METHOD FOR PREPARING TRIMETALLIC NITRIDE ENDOHEDRAL METALLOFULLERENES

(57) Abstract: A method for forming trimetallic nitride endohedral metallofullerenes having the general formula  $A_{3-n}X_nN@C_m$ , wherein A is a first metal, X is an optional second metal, n is an integer from 0-3, and m is an even integer from about 60 to about 200 is described. The method includes heating a mixture of carbon, a first metal, an option second metal, and a nitrogen containing compound in a reactor that has been sealed under vacuum at a temperature and for a time effective to form trimetallic nitride endohedral metallofullerenes.

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LOW TEMPERATURE METHOD FOR PREPARING TRIMETALLIC NITRIDE  
ENDOHEDRAL METALLOFULLERENESField of the Invention

The invention is directed to the preparation of endohedral metallofullerenes and,  
5 more particularly to a low temperature method for forming trimetallic nitride endohedral metallofullerenes.

Background of the Invention

Fullerenes are a family of closed-caged molecules made up of carbon atoms. The closed-caged molecules consist of a series of five and six member carbon rings. The  
10 fullerene molecules can contain 500 or more carbon atoms. The most common fullerene is the spherical C<sub>60</sub> molecule.

Fullerenes are typically produced by an arc discharge method using a carbon rod as one or both of the electrodes in a Krätschmer-Huffman generator. Typically the generator has a reaction chamber and two electrodes. The reaction chamber is evacuated and an inert  
15 gas is introduced in the reaction chamber at a controlled pressure. A potential is applied between the electrodes in the chamber to produce an arc discharge. The arc discharge forms a carbon plasma in which fullerenes of various sizes are produced.

Many derivatives of fullerenes have been prepared including encapsulating metals inside the fullerene cage. Metal encapsulated fullerenes are typically prepared by packing  
20 a cored graphite rod with the metal oxide of the metal to be encapsulated in the fullerene cage. The packed graphite rod is placed in the generator and arc discharged to produce fullerene products. The formation of metal encapsulated fullerenes is a complicated process and typically yields only very small amounts of the metal fullerenes.

Recently, a family of metal encapsulated fullerenes where a trimetallic nitride is  
25 encapsulated in a fullerene cages has been developed as described in U.S. Patent No. 6,303,760, herein incorporated by reference in its entirety. The trimetallic nitride

endohedral metallofullerenes have the general formula  $A_{3-n}X_nN@C_m$  ( $n = 0-3$ ) where A is a metal, X is a second trivalent metal, n is an integer from 0 to 3, and m is an even integer from about 60 to about 200. The metals A and X may be an element selected from the group consisting of a rare earth element and a group IIIB element and may be the same or different. In some embodiments, A and X may be selected from the group consisting of Scandium, Yttrium, Lanthanum, Gadolinium, Holmium, Erbium, Thulium, and Ytterbium, where A and X may be the same or different. These novel trimetallic nitride endohedral metallofullerenes are produced by introducing nitrogen gas into the Krätschmer-Huffman generator during vaporization of packed graphite rods containing corresponding metal oxides, known as the trimetallic nitride template (TNT) process.

Trimetallic nitride endohedral metallofullerenes have significant interest because of the ability to encapsulate a variety of different types of metals for a variety of applications such as superconductor materials, catalysts, nonlinear optical materials, molecular carriers for drugs, or carriers useful in missile therapy for cancer and as a radionuclide tracer. Due to the many possible applications for the endohedral metallofullerenes, additional methods for forming endohedral metallofullerenes are currently being investigated.

#### Summary of the Invention

The invention is directed to a low temperature method for forming endohedral metallofullerenes that does not require the use of a Krätschmer-Huffman generator, which typically have arc temperatures of 3000 K to 4000 K.

In accordance with a certain embodiment, the invention includes a method for forming trimetallic nitride endohedral metallofullerenes comprising the steps of charging a reactor with carbon, a nitrogen containing compound, and a metal; sealing the reactor under vacuum to form a sealed reactor; and heating the sealed reactor at a temperature and for a time effective to form a trimetallic nitride endohedral metallofullerene.

Further, the invention includes a method for forming a trimetallic nitride endohedral metallofullerene, comprising the steps of charging a reactor with a first metal, a second metal, carbon, and a nitrogen containing compound; sealing the reactor under vacuum; and heating the reactor to a temperature and for a time effective to form a trimetallic nitride endohedral metallofullerene.

### Description of the Invention

The invention is directed to a low temperature method for forming endohedral metallofullerenes, and more particularly to forming trimetallic nitride endohedral metallofullerenes. As used herein, "endohedral" refers to the encapsulation of atoms inside the fullerene cage network. Accepted symbols for elements and subscripts to denote numbers of elements are used herein. Further, all elements to the right of an @ symbol are part of the fullerene cage network, while all elements listed to the left are contained within the fullerene cage network. Under this notation,  $\text{Sc}_3\text{N}@\text{C}_{80}$  indicates that the  $\text{Sc}_3\text{N}$  trimetallic nitride is situated inside the framework of a  $\text{C}_{80}$  fullerene cage.

The method of the invention may be used to form a family of trimetallic nitride endohedral metallofullerenes representative generally as  $\text{A}_{3-n}\text{X}_n\text{N}@\text{C}_m$  ( $n = 0-3$ ) where A and X are metal atoms and m can take on even values between about 60 and about 200. To form a trimetallic endohedral metallofullerene having a cage size between about 68 carbon atoms and about 80 carbon atoms, the metal atoms may be trivalent and have an ionic radius below about 0.095 nm. When m is about 68, the metal atoms may have an ionic radius below about 0.090 nm for the  $\text{A}_3\text{N}$  endohedral species. For the  $\text{AX}_2\text{N}$  and  $\text{A}_2\text{XN}$  endohedral species, the larger atomic radius of 0.095 nm for A can be accommodated. As the size of the cage increases, the ionic radius for the metal may increase. Further, A and X may be a rare earth element, a group IIIB element, or the like. In some embodiments, A

or X may be Scandium, Yttrium, Lanthanum, Gadolinium, Holmium, Erbium, Thulium, and Ytterbium.

In accordance with an embodiment of the invention, the method for making a trimetallic nitride endohedral metallofullerene includes charging a reactor with carbon, a metal, and a nitrogen containing compound. The reactor is sealed under vacuum and heated to a temperature and for a time effective to form a trimetallic nitride endohedral metallofullerene having the general formula  $A_3N@C_m$ , where A is the metal and m ranges from about 60 to about 200.

The particular form of carbon used to charge the reactor is not particularly limited so long as the carbon will form a fullerene cage structure under the reaction conditions of the invention. The carbon may include carbon or hydrocarbon precursors with bowl-like  $sp^2$  hybridized carbon atoms that may be used as a starting template for fullerene cage formation for the endohedral metallofullerene. In certain embodiments, the carbon charged in the reactor may include an empty-caged fullerenes, including but not limited to  $C_{60}$ .

The metal that is used to charge the reactor may be a trivalent metal and may include a rare earth metal or a group IIIB metal. In certain embodiments, the metal may include, but is not limited to Scandium, Yttrium, Lanthanum, Gadolinium, Holmium, Erbium, Thulium, and Ytterbium. The metal source for supplying the metal may include, for example, the corresponding metal oxide, such as,  $Sc_2O_3$ ,  $Er_2O_3$ ,  $Ho_2O_3$ ,  $Y_2O_3$ ,  $La_2O_3$ ,  $Gd_2O_3$ ,  $Tm_2O_3$ , or  $Yb_2O_3$ .

The nitrogen containing compound provides the source of nitrogen for the trimetallic nitride complex that resides in the cage of the trimetallic nitride endohedral metallofullerene. The nitrogen containing compound is not particularly limited provided that it reacts with the metal source to form the trimetallic nitride complex for the

endohedral metallofullerene. Nitrogen containing compounds may be solids or gases so long as they react with the metal source to form the desired trimetallic nitride complex. Examples of nitrogen containing compounds include metal nitrides such as, iron nitride ( $\text{Fe}_x\text{N}$ , where  $x = 2-4$ ), group IIIB metal nitrides or rare earth metal nitrides.

5        The reactor should be charged with amounts of carbon, the metal source, and nitrogen containing compound effective to form the desired trimetallic nitride endohedral metallofullerene when the reactor is heated to a temperature ranging from about 800 K to about 1800 K. One skilled in the art will recognize that the amounts of carbon, the metal source, and the nitrogen containing compound will vary depending on the carbon being  
10    used, the metal source being used, the nitrogen containing compound being used, and the reaction conditions such as temperature, time, and pressure. In one example, 130 mgs of  $\text{C}_{60}$ , 30 mg  $\text{Sc}_2\text{O}_3$ , and 30 mg of iron nitrate were effective to form  $\text{Sc}_3\text{N}@\text{C}_{84}$  after heating at 1250 K for 24 hrs.

      Once the reactor is charged with the carbon, metal, and nitrogen containing  
15    compound, a vacuum is pulled on the reactor and the reactor is sealed such that the contents of the reactor are now under vacuum. The sealed reactor is then heated at a temperature and for a time effective to form trimetallic nitride endohedral metallofullerene compounds. The reactor may be heated to a temperature ranging from about 800 K to about 1800 K. In one embodiment, the reactor is heated to about 1250 K. The time  
20    required to form the trimetallic nitride endohedral metallofullerene compounds may vary depending on the reactants used to charge the reactor, the temperature used to heat the reactor, and other conditions known to those skilled in the art. In certain embodiments, when the temperature is about 1250 K, a reaction time of about 24 hours is sufficient to form a trimetallic nitride endohedral metallofullerene. The reactor may be a quartz tube,  
25    but can be made from any suitable material that can withstand the above described reaction

conditions. The reactor should be able to hold a vacuum during heating and must be able to withstand the reaction temperatures. Further, the material of the reactor should not react with the carbon, metal or metals, or the nitrogen containing compound.

When the encapsulation of more than one type of metal in the fullerene cage is  
5 desired, a second metal may be added to the reactor. In this embodiment, the reactor is charged with carbon, a first metal, a second metal, and a nitrogen containing compound. The reactor is sealed under vacuum and heated to the desired temperature for a time effective to form the trimetallic nitride endohedral metallofullerene.

The carbon and nitrogen containing material should have the same characteristics  
10 as those described above. Further, the first metal and second metal, as described above, may be a trivalent metal and may include a rare earth metal or a group IIIB metal. In certain embodiments, the first metal and second metal may include, but are not limited to Scandium, Yttrium, Lanthanum, Gadolinium, Holmium, Erbium, Thulium, and Ytterbium. While the first metal and second metal may be selected from the same group of metals, in  
15 some embodiments, the first metal and the second metals are different to form a trimetallic nitride endohedral metallofullerene having the general formula  $A_{3-n}X_nN@C_m$ , where A is the first metal, X is the second metal, n ranges from 1 to 3, and m ranges from about 60 to about 200. The first metal and the second metal are added to the reactor in the form of a metal source, which may include, but is not limited to, the respective metal oxide.  
20 Representative metal oxides may include, but are not limited to,  $Sc_2O_3$ ,  $Er_2O_3$ ,  $Ho_2O_3$ ,  $Y_2O_3$ ,  $La_2O_3$ ,  $Gd_2O_3$ ,  $Tm_2O_3$ , or  $Yb_2O_3$ . The ratio of first metal oxide to second metal oxide may range from about 1:1 to about 3:1 depending on the ratio of metals desired in the endohedral metallofullerene.

The reactor should be charged with amounts of carbon, the first metal source, the  
25 second metal source, and nitrogen containing compound effective to form the desired



trimetallic nitride endohedral metallofullerene when the reactor is heated to a temperature ranging from about 800 K to about 1800 K. One skilled in the art will recognize that the amounts of carbon, the first metal source, the second metal source, and the nitrogen containing compound will vary depending on the carbon being used, the first and second  
5 metal sources being used, the nitrogen containing compound being used, and the reaction conditions such as temperature, time, and pressure.

After the reactants have been heated for a sufficient amount of time and at a sufficient temperature, the reactor may be opened and the resulting soot containing the reaction products may be removed. Isolation of the trimetallic nitride endohedral  
10 metallofullerenes consists of using carbon disulfide or toluene to extract the soluble fullerenes from the soot. All members of the trimetallic nitride endohedral metallofullerenes,  $\text{Er}_{3-n}\text{Sc}_n\text{N@C}_{80}$ ,  $\text{Ho}_{3-n}\text{Sc}_n\text{N@C}_{80}$ ,  $\text{Y}_{3-n}\text{Sc}_n\text{N@C}_{80}$ ,  $\text{Gd}_{3-n}\text{Sc}_n\text{N@C}_{80}$  and  $\text{La}_{3-n}\text{Sc}_n\text{N@C}_{80}$  where  $n = 0-3$ , are extractable in carbon disulfide except  $\text{Yb}_{3-n}\text{Sc}_n\text{N@C}_{80}$  and  $\text{Tm}_{3-n}\text{Sc}_n\text{N@C}_{80}$  ( $n = 0-3$ ).

15 While the separation method is described for  $\text{A}_{3-n}\text{X}_n\text{N@C}_{80}$  it is also applicable to other trimetallic nitride endohedral metallofullerenes such as  $\text{A}_{3-n}\text{X}_n\text{N@C}_{68}$  and  $\text{A}_{3-n}\text{X}_n\text{N@C}_{78}$ . The separation methods are the same as those described in U.S. Patent No. 6,303,760, herein incorporated by reference in its entirety.

In accordance with certain embodiments, trimetallic nitride endohedral  
20 metallofullerenes having the general formula  $\text{A}_{3-n}\text{X}_n\text{N@C}_m$ , are produced using the above described low temperature method. Using the method of the invention reduces the temperature at which trimetallic endohedral metallofullerenes are produced when compared to the high arc temperature of the Krätschmer-Huffman generator.

The present invention is illustrated in the following examples. The examples are provided for illustration purposes and should not be construed as limiting the scope of the present invention.

Example

5 In a quartz tube, 150 mg of  $C_{60}$ , 30 mg of iron nitride ( $Fe_xN$ ,  $x=4-2$ ), and 30 mgs of scandium oxides ( $Sc_2O_3$ ) were heated and sealed under vacuum. The tube was subsequently placed in a tube furnace at 1250 K for 24 hours. At the end of this period, the tube contents were removed and the soot from the tube was extracted with  $CS_2$  and the soluble fraction of fullerenes and endohedral metallofullerenes were analyzed by negative-  
10 ion mass spectrometry and purified by high performance liquid chromatography. Both the chromatographic retention time and mass spectrometry data clearly identify the endohedral metallofullerene  $Sc_3N@C_{80}$  as the major product. Several other empty-cages were also produced, e.g.,  $C_{70}$  and  $C_{84}$ . Non-nitrogen containing endohedral metallofullerenes by-products, e.g.,  $Sc_2@C_{84}$ , did not appear in the soot resulting from the reaction.

15 It will therefore be readily understood by those persons skilled in the art that the present invention is susceptible to broad utility and application. Many embodiments and adaptations of the present invention other than those herein described, as well as many variations, modifications and equivalent arrangement, will be apparent from or reasonably suggested by the present invention and the foregoing description thereof, without departing  
20 from the substance or scope of the present invention.

Accordingly, while the present invention has been described herein in detail in relation to certain embodiments, it is to be understood that this disclosure is only illustrative and exemplary of the present invention and is made merely for purposes of providing a full and enabling disclosure of the invention. The foregoing disclosure is not  
25 intended or to be construed to limit the present invention or otherwise to exclude any such

other embodiments, adaptations, variations, modifications and equivalent arrangements,  
the present invention being limited only by the claims and the equivalents thereof.

## CLAIMS

What is claimed is:

1. A method for forming trimetallic nitride endohedral metallofullerenes,  
comprising the steps of:
  - 5 charging a reactor with carbon, a nitrogen containing compound, and a metal;  
sealing the reactor under vacuum to form a sealed reactor;  
heating the sealed reactor at a temperature and for a time effective to form a  
trimetallic nitride endohedral metallofullerene.
2. The method of claim 1 wherein the metal is a rare earth element or a group  
10 IIIB element.
3. The method of claim 1 wherein the metal includes a metal selected from the  
group consisting of Scandium, Yttrium, Lanthanum, Gadolinium, Holmium, Erbium,  
Thulium, and Ytterbium.
4. The method of claim 1 wherein the nitrogen containing compound is a  
15 metal nitride.
5. The method of claim 1 wherein the sealed reactor is heated to a temperature  
ranging from about 800 K to about 1800 K.
6. The method of claim 1 wherein the carbon includes C<sub>60</sub>.
7. The method of claim 1 wherein the metal is supplied in the form of a metal  
20 oxide.
8. A method for forming a trimetallic nitride endohedral metallofullerene,  
comprising the steps of:

charging a reactor with a first metal, a second metal, carbon, and a nitrogen  
containing compound;  
sealing the reactor under vacuum; and  
heating the reactor to a temperature and for a time effective to form a trimetallic  
5 nitride endohedral metallofullerene.

9. The method of claim 8 wherein the first metal is a rare earth element or a  
group IIIB element, and the second metal is a rare earth element or a group IIIB element.

10. The method of claim 8 wherein the first metal is selected from the group  
consisting of Scandium, Yttrium, Lanthanum, Gadolinium, Holmium, Erbium, Thulium,  
10 and Ytterbium; and the second metal is different from the first metal and selected from the  
group consisting of Scandium, Yttrium, Lanthanum, Gadolinium, Holmium, Erbium,  
Thulium, and Ytterbium.

11. The method of claim 8 wherein the nitrogen containing compound is a  
metal nitride.

15 12. The method of claim 8 wherein the first metal is a first metal oxide and the  
second metal is a second metal oxide.

13. The method of claim 8 wherein the first metal and the second metal are  
different.

14. The method of claim 8 wherein the carbon includes C<sub>60</sub>.

20 15. The method of claim 8 wherein the reactor is heated to a temperature  
ranging from about 800 K to about 1800 K.

16. The method of claim 8 wherein the trimetallic nitride endohedral metallofullerene has the formula  $A_{3-n}X_nN@C_m$ , wherein A is the first metal, X is the second metal, n is an integer from 1-3, and m is an even integer from about 60 to about 200.